Influence of hydrolysis temperature on the hydrolysis products of aluminium alkoxides

R. I. ZAKHARCHENYA, T. N. VASILEVSKAYA A. F. loffe Physico-Technical Institute, Russia

The influence of hydrolysis on the hydrolytic polycondensation of aluminium alkoxides was studied. Two mechanisms of hydrolysis which give two different products are proposed for this process. Structural transformations of the resultant condensates, i.e. boehmite, (γ -AlOOH), the product of hot-water hydrolysis, and gibbsite Al (OH)₃, the product of cold water hydrolysis, have been investigated in temperature range 20–1300 °C. An explanation was offered for the variations in the α -Al₂O₃ transformations of the condensate produced by room temperature hydrolysis.

1. Introduction

Physicochemical studies of sol-gel conversion are of great interest due to the importance of the process in modern technology. In these processes, particular attention is paid to the reaction in which the reagents are metal alkoxides. Recent publications have been devoted to the selection of suitable solvents and reagents, discussion of the mechanism and kinetics of the hydrolysis process, electrolytic behaviour of the sol, and sintering of gels into final ceramic products. A complete review devoted to the physicochemical study of metal alkoxide based sol-gel process has recently been published [1]. Despite the abundance of works devoted to silicon alkoxide hydrolysis, only a few works deal with the hydrolytic polycondensation of aluminium alkoxides [2–4].

In this work the influence of temperature was studied on the hydrolysis of the aluminium alkoxides Al $(OR)_3$ with bulky alkyl groups (R) where $R = Pr^i$, Bu^s , Bu^i . The reaction products have been investigated by X-ray powder diffraction (XRD) and differential thermal analysis (DTA) techniques.

These studies were prompted by observations of the unreproducibility of the thermal effect (which may be exo- or endo-, or without thermal effect) under α -Al₂O₃ transformation of the hydrolysis product obtained by room-temperature hydrolysis of the alk-oxides. It is technologically important to determine the origin of this unreproducibility, especially as this does not occur when the hydrolysis is performed at 80 °C.

2. Experimental procedure

To determine the effect of temperature on the composition of the hydrolysis products, high-purity aluminium isopropoxide, secondary and tertiary aluminium butoxides were used. The hydrolysis was carried out with bidistilled and deionized water. The alkoxide: water molar ratio was kept at 1:100 in all cases. The precipitates obtained were not peptized. These measures were taken to diminish the role of impurities in the aluminium hydroxide and aluminium oxide structures during the sol-gel and calcination processes.

The precipitates obtained by hydrolysis of the aluminium alkoxides (Al $(OC_3H_7^i)_3$, Al $(OC_4H_9^s)_3$ and Al $(OC_4H_9^t)_3$ under temperature ranges 80–100, 20 ± 5 and 0–5 °C were washed out from the alcohol. At the end of this procedure, precipitates were dried in the presence of CaCl₂ at temperatures corresponding to the hydrolysis temperatures. The precipitates dried in this way were then heated at 5 °C min⁻¹ to 1300 °C in air. Samples for XRD analysis were taken in the 20–1300 °C interval at 50 °C steps.

3. Results and discussion

Structural investigations performed using XRD are presented in Figs 1–3. This series of three X-ray patterns shows the systematic influence of hydrolysis temperature on the initial composition of hydrolysis products, as well as α -Al₂O₃ transformations on heating. The XRD measurements were carried out at 2 Θ 10–90° using CuK_{α} (λ = 1.54) radiation from powders pressed on a PMMA base. Tables I and II give the relative intensities (I_i/I_{max}) and calculated *d*-spacing [5] for the products of hydrolysis at 80–100 °C and 0–5 °C.

These results show that aluminium monohydroxide (boehmite) resulting from hot-water hydrolysis appears to be unique stable phase, as previously found by Yoldas [2]. As seen in pattern 1 of Fig. 1, the number and positions of the XRD peaks of this phase are in accord with the data published in [6]. It should be noted that all the Bragg reflections are more intense than the standard data. This fact demonstrates that boehmite exists here in the well-crystallized state. A small shift of the most intensive peak with d = 0.630-0.632 nm in the boehmite crystal frame, in the 80-150 °C temperature range, may be explained by the presence of large numbers of water molecules localized between layers of the octahedra [AIO₆] from



Figure 1 Series of XRD patterns indicating consequence of boehmite [hydrolysis product of the aluminium alkoxides by hot-water (80–100 °C)] phase transformations into corundum under heating: 1, pseudoboehmite (80–100 °C); 2, boehmite (150–400 °C); 3, transition state (450–550 °C); 4, γ –Al₂O₃ (550–850 °C); 5, δ –Al₂O₃ (900–950 °C); 6, Θ –Al₂O₃ and α –Al₂O⁽¹⁾₃ (1000–1150 °C); 7, α –Al₂O₃.

which the boehmite lattice is built. This excess water leads to the distortion of the boehmite structure. This structure (with d = 0.630-0.670 nm) has been described as "pseudoboehmite" [7]. After heating at 200 °C, the peak position with 0.614 nm strictly corresponds to the boehmite form (pattern 2).

Curve (1) of Fig. 4 represents the differential thermal analysis (DTA) data of boehmite. The first endothermic effect at curve DTA-1 with a minimum at 125 °C corresponds to the drying process that is accompanied by the removal of all adsorbed water molecules from the porous space of the boehmite lattice. The temperature interval of this effect is 70-150 °C. The weight losses during this process are about 12-30%. This value characterizes the large specific surface of the γ -AlOOH. The boehmite specific surface can vary from 80 up to 350 m² g⁻¹ depending on hydrolysis conditions. The second endothermic effect (425-550 °C) with a minimum at about 500 °C appears in curve DTA-1 as a single slightly asymmet-



Figure 2 Series of XRD patterns indicating the phase composition of the hydrolysis product obtained from aluminium alkoxides under hydrolysis at room temperature $(20 \pm 5 \,^{\circ}\text{C})$ and the polymorphous transformations into corundum of the product under heating up to $1300 \,^{\circ}\text{C}$: 1, Al (OH)₃⁽¹⁾; AlOOH⁽²⁾ and γ -Al₂O₃⁽³⁾ (20–150 $\,^{\circ}\text{C}$); 2, transition state (200–500 $\,^{\circ}\text{C}$); 3, γ -Al₂O₃ (500–900 $\,^{\circ}\text{C}$); 4, δ -Al₂O₃ (950–1000 $\,^{\circ}\text{C}$); 5, θ -Al₂O₃ (1050–1100 $\,^{\circ}\text{C}$); 6, α -Al₂O₃ and θ -Al₂O₃ (1150 $\,^{\circ}\text{C}$). Peak intensities of the θ -alumina phase are 10% less those of α -alumina phase. 7, α -Al₂O₃ and θ -Al₂O₃ (1200 $\,^{\circ}\text{C}$); 8, α -Al₂O₃ (1250 $\,^{\circ}\text{C}$).

ric broad band corresponding to the boehmite transformation into γ -Al₂O₃. The weight loss during this process is about 13.2%. This value is slightly smaller than that corresponding to the reaction:

$$2\gamma - AlOOH \rightarrow Al_2O_3 + H_2O$$
 (1)

However the loss of the remaining water molecules (about 2%) cannot be registered reliably up to the ultimate temperature of 1300 °C. Thus the present results concerning hot water hydrolysis of the aluminium alkoxides coincide with those described in [2 and 3], and differ from data for ambient water hydrolysis [7]. It has been shown by electron microscopic methods [3, 8] that aluminium alkoxide hydrolysis performed at room temperature gives an amorphous monohydroxide which, with time, transforms to crystalline aluminium trihydroxide Al (OH)₃ in the bayerite form [2].



Figure 3 Series of XRD patterns indicating the gibbsite (hydrolysis product of aluminium alkoxides at 0–5 °C) phase transformations into corundum under heating: 1, gibbsite–Al(OH)₃ (0–5 °C); 2, bayerite– γ –Al (OH)₃ (50–300 °C); 3, transition state (350–400 °C); 4, γ –Al₂O₃ (450–950 °C); 5, δ –Al₂O₃ (1000–1100 °C); 6, θ –Al₂O₃ and α –Al₂O⁽¹⁾ (1150–1250 °C); 7, α –Al₂O₃ (1300 °C).

Results concerning the phase composition of the products of aluminium alkoxide hydrolysis performed at room temperature are shown in Fig. 2. It can be seen that there are several phases in the hydrolysis product in this case. Sharp, strong peaks belong to the crystalline phase of Al (OH)₃ in the gibbsite form. The broad reflections in the same pattern belonging to the other phase can be ascribed to pseudoboehmite, which exists (judging by the peak shape) in an amorphous state. The XRD pattern of the well-crystallized boehmite γ -AlOOH, is depicted in Fig. 2 by the dashed line. In this precipitate there is another phase which becomes predominant at temperatures just above 200 °C. This phase corresponds to the γ -Al₂O₃, low temperature modification of alumina. (It should be noted that in the case of the hot-water hydrolysis product this phase appears only at temperatures above 450 °C.) From XRD patterns 2-4 in Fig. 2, it can be seen that transformation of the inhomogeneous condensate into γ -Al₂O₃ completely terminates at 500 °C. These results are in agreement with the DTA data (not presented in Fig. 4). According to this data, the temperature interval of the second endothermic effect, which corresponds to the transition of the inhomogeneous condensate into y-alumina, expands from 185 up to 500 °C and has no legible minimum at the DTA-curve. The first endothermic peak at the same curve is also broad, explained by the loss of the crystallohydrated water by the Al (OH)₃ phase and adsorbed water by the AlOOH phase. The loss of weight by the inhomogeneous condensate during heating up to conversion into γ -Al₂O₃ is strongly dependent on its phase composition.

As formation of Al(OH)₃ occurs at hydrolysis below 80 °C, a third hydrolysis was carried out at near 0 °C by bidistilled water obtained from melted ice. The result of this type of hydrolysis is presented in Fig. 3. The only product of the aluminium alkoxide hydrolysis at 0-5 °C is the well-crystallized Al(OH)₃ in the gibbsite form. It should be emphasized that the intensities of the two strongest peaks are reversed above 50 °C, while values of the interplanar distances corresponding to these peaks remain constant. The XRD pattern 2 belongs to the bayerite structure, i.e., γ -Al (OH)₃ [6]. From this we can conclude that the gibbsite and the bayerite crystal forms differ only in the water content in their lattices.

The same changes in peak intensity are observed in the gibbsite phase of the product of room temperature hydrolysis. From these observations, we may conclude that the gibbsite is a low-temperature modification of the bayerite structure. The bayerite is stable in the $50-300^{\circ}$ temperature range, existing as the only phase in the case of hydrolysis at 0-5 °C. The XRD analysis shows that the bayerite transforms into the first lowtemperature modification of alumina without creation of an intermediate monohydroxide form, (as a single form), as would be the case if the water was lost in stages, e.g.:

$$\gamma - \text{Al}(\text{OH})_3 \rightarrow \gamma - \text{AlOOH} + \text{H}_2\text{O}$$
 (2)

The initial oxide phase corresponding to γ -Al₂O₃ appears in a narrow temperature range, 300-350 °C, directly from the trihydroxide, as seen in XRD pattern 3 (Fig. 3). This is manifested in the broadening of the peaks and in the reduction of their number. However, formation of the boehmite structure can be identified by the observation of new narrow peaks at XRD pattern 4, which corresponds to transition state of the bayerite. The positions of the narrow peaks are in good agreement with that in the boehmite structure. Thus these two processes appears to go simultaneously as a chain reaction:

$$4\gamma - \text{Al}(\text{OH})_{3} \rightarrow [\gamma - \text{Al}_{2}\text{O}_{3}^{*}2\gamma - \text{Al}\text{OOH}] + 5\text{H}_{2}\text{O} \rightarrow 2\gamma - \text{Al}_{2}\text{O}_{3} + 7\text{H}_{2}\text{O}$$
(3)

These results are in agreement with DTA data shown in Fig. 4 by curve DTA-2. The loss of weight at the first endothermic effect with a minimum at 100 °C is ~ 3.3%. According to this result, the crystallohydrate form of the bayerite is γ -Al (OH) 0.15 H₂O. In the temperature range 290-380° C, the second endothermic effect corresponding to the phase transformation of the bayerite into γ -alumina is observed. This effect is manifested as a twin unresolved endothermic peak with minima at 320 and 330 °C at curve DTA-2. The 32% weight loss during this process is slightly smaller (the same is seen in the case of the boehmite trans-

TABLE I Interplanar distances (d) and relative intensities $(I_i/I_{max})^{\dagger}$ of peak positions at XRD patterns (Fig. 1)

80–100 °C Alooh		150-400 °C γ-AlOOH		550–850 °C γ–Al ₂ O ₃		900–950 °C δ–Al ₂ O ₃		$1000-1150 ^{\circ}\text{C}$ ($\theta + \alpha^*$)-Al ₂ O ₃		1200–1300 °C α–Al ₂ O ₃	
0.632	100	0.614	100	0.609	17	0.450	10	0.450	10	0.343	61
0.313	61	0.314	91	0.250	33	0.283	41	0.345*	11	0.252	90
0.234	70	0.233	74	0.246	40	0.271	75	0.281	52	0.235	40
0.184	82	0.197	13	0.240	50	0.243	54	0.271	98	0.2065	100
0.176	12	0.184	99	0.231	43	0.224	31	0.253*	31	0.173	44
0.165	13	0.176	18	0.226	45	0.198	62	0.243	70	0.172	31
0.144	25	0.166	19	0.196	75	0.194	31	0.237*	24	0.1591	84
0.143	32	0.144	30	0.152	18	0.154	21	0.230	45	0.1588	55
0.139	12	0.143	40	0.139	100	0.149	17	0.224	41	0.140	32
0.138	10	0.130	32			0.145	18	0.207*	14	0.139	19
0.130	27	0.113	15			0.138	100	0.201	61	0.137	50
0.113	12							0.198	32	0.136	30
								0.194	16	0.1233	14
								0.190	34	0.1229	12
								0.179	14		
								0.160*	14		
								0.153	26		
								0.150	14		
								0.148	15		
								0.145	26		
								0.142	17		
								0.140*	53		
								0.138	100		
								0.129	17		
								0.128	12		

[†]Bragg reflections with intensities less than 10% are not included in the table.

TABLE II Interplanar distances (d) and relative intensities $(I_i/I_{max})^{\dagger}$	[†] of pea	k positions at XRD) patterns (Fig.	3)
---	---------------------	--------------------	--------------	------	----

0–5 °C		50–300 °C		450–950 °C		1000–1100 °C		1150–1250 °C		1300 °C	
Al (OH) ₃		γ-Al (OH) ₃		$\gamma - Al_2O_3$		$(\delta + \theta) - Al_2O_3$		$(\theta + \alpha)$ -Al ₂ O ₃		$\alpha - Al_2O_3$	
<i>d</i> (nm)	I/I (%)	d (nm)	I/I (%)	d (nm)	I/I (%)	<i>d</i> (nm)	I/I (%)	d (nm)	I/I (%)	<i>d</i> (nm)	I/I (%)
0.467	48	0.471	57	0.446	12	0.660	10	0.446	18	0.343	55
0.461	97	0.465	100	0.294	17	0.446	17	0.280	57	0.252	82
0.427	79	0.433	73	0.276	26	0.269	61	0.269	71	0.235	38
0.317	33	0.318	24	0.250	26	0.253	22	0.253	21	0.2065	100
0.220	100	0.221	80	0.243	37	0.248	20	0.241	70	0.173	42
0.171	43	0.171	30	0.240	45	0.241	63	0.230	52	0.159	98
0.145	17	0.145	11	0.237	62	0.234	25	0.223	39	0.140	34
0.144	11			0.233	36	0.229	43	0.199	57	0.137	56
0.133	11			0.196	78	0.224	38	0.194	16	0.1234	13
0.132	14			0.151	22	0.199	56	0.189	30	0.1230	11
				0.139	100	0.195	23	0.178	13		
						0.192	22	0.153	29		
						0.190	23	0.147	25		
						0.178	12	0.144	31		
						0.177	10	0.140	46		
						0.153	26	0.138	100		
						0.152	19	0.129	13		
						0.148	23	0.128	14		
						0.144	27				
						0.140	100				
						0.138	55				
				-		0.128	12				

[†]Bragg reflections with intensities less than 10% are not included in the table.

formation) than that required according to the reaction

pond strictly to reactions (1) and (4) only at their transformation into the α -Al₂O₃.

$$2\gamma - \text{Al} (\text{OH})_3 \rightarrow \gamma - \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$
 (4)

The weight loss by the boehmite and bayerite corres-

It should be emphasized that the prehistory of the phase transformations into γ -Al₂O₃ and into α -Al₂O₃ are not the same for γ -AlOOH and γ -Al



Figure 4 DTA curves of boehmite (1) and bayerite (2). Rate of heating, $7.5 \,^{\circ}\text{C min}^{-1}$.

 $(OH)_3$. As seen from the XRD data and from the DTA analysis, the phase transformation of the boehmite into γ -alumina is shifted to higher temperatures by 150 °C above that of the bayerite, and 250 °C above that of the bayerite–boehmite mixture. These phase transformations are accompanied not only by the loss of water molecules but also by changes in the aluminium coordination number:

[AlO₆] (all aluminium hydroxides) \rightarrow [AlO₄] (all low-temperature modifications of alumina) \rightarrow [AlO₆] (corundum, α -Al₂O₃)

and with structural transformations:

monoclynic (boehmite bayerite)
$$\rightarrow$$
cubic
(γ -Al₂O₃) \rightarrow tetragonal (δ -Al₂O₃) \rightarrow monoclynic
(θ -Al₂O₃) \rightarrow trigonal (α -Al₂O) (5)

In addition, the boehmite phase transformation into γ -Al₂O₃ strongly differs from that of bayerite. From XRD pattern 3 (Fig. 1), corresponding to the temperature range of the second endothermic effect on the DTA-1 curve of Fig. 4, very narrow peaks can be seen along with broad reflections of the γ -alumina phase. This phase, which appears during the formation of the phase γ -Al₂O₃, cannot be attributed reliably to known modifications of aluminium hydroxides and oxides. It can be proposed that in this transition state the layered structure of boehmite undergoes distortion, which manifests itself in the disappearance of the peak with d = 0.614 nm and by shifts in the narrow peak positions. The boehmite structure is built from the double-folded layers of the [AlO₆] octahedra. These layers are connected by the hydrogen bonds. The loss of water under heating of the boehmite leads to formation of Al-O-Al bridge bonds. Thus the formation of gamma-alumina structure from boehmite goes through the transition state according to the following scheme:

 3γ -Alooh- $\rightarrow\gamma$ -Al₂O₃ + [β -Alooh] + H₂O (6)

From comparative analysis of the XRD patterns for aluminium oxides and hydroxides it can be seen that the 0.614 nm peak is absent in the diaspore structure, ascribed as β -AlOOH or Al₂O₃H₂O in [6]. Moreover, the strongest Bragg reflections of the diaspore structure [0.399 nm (100%), 0.232 nm (56%) and 0.211 nm (52%)] are similar to those which appear as the narrow peaks at XRD pattern 3 (Fig. 3) corresponding to the boehmite transition state into γ -Al₂O₃:0.324 nm (100%), 0.231 nm (72%) and 0.199 nm (43%). On the basis of these data we conclude that the transformation of the boehmite into γ -alumina goes through the formation of a quasidiaspore crystal lattice.

Thus the boehmite, γ -AlOOH, and the bayerite, γ -Al (OH)₃, behave differently during the dehydration to γ -alumina. However, as our studies have shown, both go through a series of low-temperature polymorphisms of alumina before transforming into corundum, as described earlier.

Nevertheless, there is a difference between the alumina polymorphic transformations beginning from the γ -Al₂O₃, obtained from the bayerite and from the boehmite. This difference can be explained by the diversity in the crystal grain size in both products of γ -alumina. From the width of peaks on the XRD pattern 4 presented in Figs 1 and 3, it can be seen that the crystal grain size of the γ -alumina obtained from the γ -AlOOH is smaller than those from γ -Al (OH)₃. One conclusion that can be drawn is that the dispersity stores information about the precursor's nature. The main reason for the observed unreproducibility of the thermal effect of the phase transformation into corundum (for products obtained by room-temperature hydrolysis) appears to be the difference in the temperature ranges of polymorphous transformations for boehmite and bayerite, due to the diversity in the crystal grain size of gamma-alumina produced from these sources. Due to this difference, γ -Al₂O₃ obtained from inhomogeneous condensates behaves as a two-phase system. This fact manifests itself one more time on three last XRD patterns at Fig. 2. From these curves we can see that the crystallization of corundum in the first phase significantly perturbs the lattice of the second phase, θ -Al₂O₃. The evidence of this is the strong reduction of the peak intensities observed at XRD pattern 6. In the next temperature range (see XRD pattern 7, Fig. 2) both phases θ -Al₂O₃ and α -Al₂O₃ are identified again, as we believe, due to the relaxation of the system. It is noteworthy that this relaxation takes place in the presence of corundum, which plays the role of nucleation centres affecting the energetics of the α -Al₂O₃ transformation. It is well known that the addition of such oxides as α -Al₂O₃, α -Fe₂O₃, MgO etc. to γ -alumina decreases the temperature of its conversion into corundum and the sintering temperature of the corundum [9, 10]. The α alumina transformations of both chemically pure forms of the aluminium hydroxides i.e. the boehmite and the bayerite, are always accompanied by an exothermic DTA peak at 1250 ± 50 °C, as seen in Fig. 4. Thus we can conclude that the inhomogeneity of the hydrolysis products derived from localized variations in temperature during hydrolysis is the main reason for the difference in the consequent structural transformations.

In these studies, the purity of the precursors provides almost full exclusion of cation and anion impurities. Thus the charge of anionic frames of the alumina, built from [AlO₄] tetrahedra sharing common corners, must be compensated by the positive charge provided by H^+ (H_3O^+) or Al⁺³ cations. Firstly, this situation leads to an increase in the defect concentration in the alumina structures. These defects can play an important role in the relaxation of stresses, allowing the production of sufficiently large monolithic samples of porous alumina without cracks. Secondly, the absence of cations which stabilize low-temperature modifications of alumina leads to hindrance of the phase transformations at heating. Due to this hindrance, we can observe the sequence of polymorphous There are at least three channels of further reactions. The first channel is the reverse reaction; the second and third channels are the formation of the aluminium monohydroxide, AlOOH and trihydroxide, Al (OH)₃, bonding to hot- and cold-water hydrolysis. The next step in structural evolution, in the case of hot-water hydrolysis, involves the removal of organics as alcohol molecules. This process, due to an increase of a positive charge at the aluminium atom, leads to the creation of more stable complex. Such an increase in positive charge at the Al atom promotes strengthening of the aluminium–oxygen bonds by shifting the electron density to the Al atom. A significant increase in positive charge at the carbon atom connected to the alkyl groups occurs:

$$\begin{bmatrix} RO & OR \\ \land / \\ Al \\ \vdots \\ O: H^{+} \\ R \end{bmatrix} \stackrel{*}{\longrightarrow} \begin{bmatrix} RO \stackrel{+}{\longrightarrow} Al \stackrel{+}{\longrightarrow} OR \end{bmatrix} OR \stackrel{*}{\longrightarrow} e^{Al} \stackrel{*}{\longrightarrow} OR \stackrel{*}{\longrightarrow} e^{CH_{3}} \stackrel{CH_{3}}{\longrightarrow} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} e^{CH_{3}} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} e^{CH_{3}} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} e^{CH_{3}} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} OH \stackrel{*}{\longrightarrow} e^{CH_{3}} OH \stackrel{*}{\longrightarrow} O$$

conversions of aluminium oxides and understand the reason for the shift of these conversion temperatures to higher values.

The chemical properties of metal alkoxides are determined by the nature of the metals and organic

This allows OH^- groups to attack the carbon atom possessing a positive charge. As a result of this action, the next ester group splits away and the strongest aluminium-oxygen bond (Al = O) is formed. This splitting occurs via cleavage of the oxygen-carbon bond according to the following scheme:

$$RO = Al = O + ROH \qquad (9)$$

groups (R). In the aluminium alkoxides Al (OR)₃ used in these experiments, the alkyl groups were $R = C_3H_7^i$, $C_4H_9^s$ and $C_4H_9^t$. In these compounds, Al–O The splitting of the third ester group may go through two competitive channels, which cannot change the final product:

bonds are essentially covalent due to the large + J inductive effect of alkyl groups, aluminium possibly exhibiting amphoteric properties. In addition, the positive charge of a relatively small aluminium atom is shielded by organic groups, thus hindering the nucleophylic attack of OH⁻ ions. It is likely that aluminium alkoxide hydrolysis is initiated by a proton attack on the lone electron pairs of oxygen in OR groups, according to the following equation:





These two competitive processes can be shown by the following scheme:

$$AI(OR)_{3} + H_{2}O \longrightarrow \begin{bmatrix} RO & OR \\ AI \\ I \\ RO & H^{+} \end{bmatrix} \stackrel{*}{\longrightarrow} \begin{bmatrix} RO & OR \\ AI \\ AI \\ ROH^{+} & OH^{-} \end{bmatrix} \stackrel{*}{\longrightarrow} \begin{bmatrix} RO & OR \\ AI \\ ROH^{+} & OH^{-} \end{bmatrix} \stackrel{*}{\longrightarrow} \stackrel{*}{\longrightarrow} \begin{bmatrix} RO & OR \\ AI \\ ROH^{+} & OH^{-} \end{bmatrix} \stackrel{*}{\longrightarrow} \stackrel{*}{\longrightarrow}$$

$$RO-AI-OR + \downarrow ROH$$
(11)

As can be seen from Equation 11 the hydrolysis of the aluminium alkoxides by cold water occurs as a chain of the consequent replacement of alkyl groups by OH groups. However, alcohol remains in the reaction environment during the hydrolysis process and slows this reaction. It should be noted that the creation of the Al-OH bond, even at low temperatures, is thermodynamically preferable to the Al-OR bond. Thus each OR group of precursors is replaced step-bystep by the OH⁻ group of water with formation of the Al $(OH)_3$.

4. Conclusions

ÓН

From this study we can conclude that the main reason for the observed unreproducibility in the thermal effect of phase transformation into corundum, in the case of room-temperature hydrolysis, appears to be the inhomogeneous obtained condensate. In this condensate there are phases of boehmite and bayerite which give $\gamma - Al_2O_3$ with different dispersity. Due to this difference, the γ -alumina behaves as a two-phase system. For these two phases there is a difference in the temperature intervals of polymorphous transformations. The thermal effect under phase transformation into corundum strongly depends on the phase composition of the hydrolysis product. As the hydrolysis reaction is exothermic and the uniformity is mixing-dependent, localized variations in temperature occur. The α -Al₂O₃ transformations of the bayerite and boehmite pure forms always occur with exothermic effects.

Acknowledgement

The authors wish to express their sincere thanks to Dr B. E. Yoldas for critical review of the manuscript and helpful comments.

References

- 1. R. C. MEHROTRA, J. Non-Cryst. Solids 121 (1990) 1.
- 2. B. E. YOLDAS, J. Appl. Chem. Biotech. 23 (1973) 803.
- Idem, Amer. Ceram. Bull. 54 (1975) 289. 3
- R. NASS and H. SCHMIDT, J. Non-Cryst. Solids 121 (1990) 4. 329.
- G. BROWN (ed) "The X-ray identification and structures of 5. clay minerals" (Mineralogical Society Clay Minerals Group, London 1961).
- 6. ANON., "Powder Diffraction Fine Inorganic Phase Alphabetical Index (Chemical & Mineral Names)" (JCPOS International Centre for Diffraction Data, Pennsylvania, 1985).
- 7. D. PAPEE, R. FERTIAN and R. BIAIS, Bull. Soc. Chem. France (1958) 1301.
- G. BYE and J. G. ROBINSON, Kolloid Z. 53 (1964) 198. 8.
- J. L. MCARDLE and G. L. MESSING, J. Amer. Ceram. Soc. 9. 69 (1986) 98.
- 10 F. W. DYNYS and J. W. HALLORAN, in "Ultrastructure processing of Ceramics, Glasses & Composites", edited by L. L. Hench and D. R. Ulrich (New York, 1984) p. 142.

Received 29 January 1992 and accepted 31 August 1993